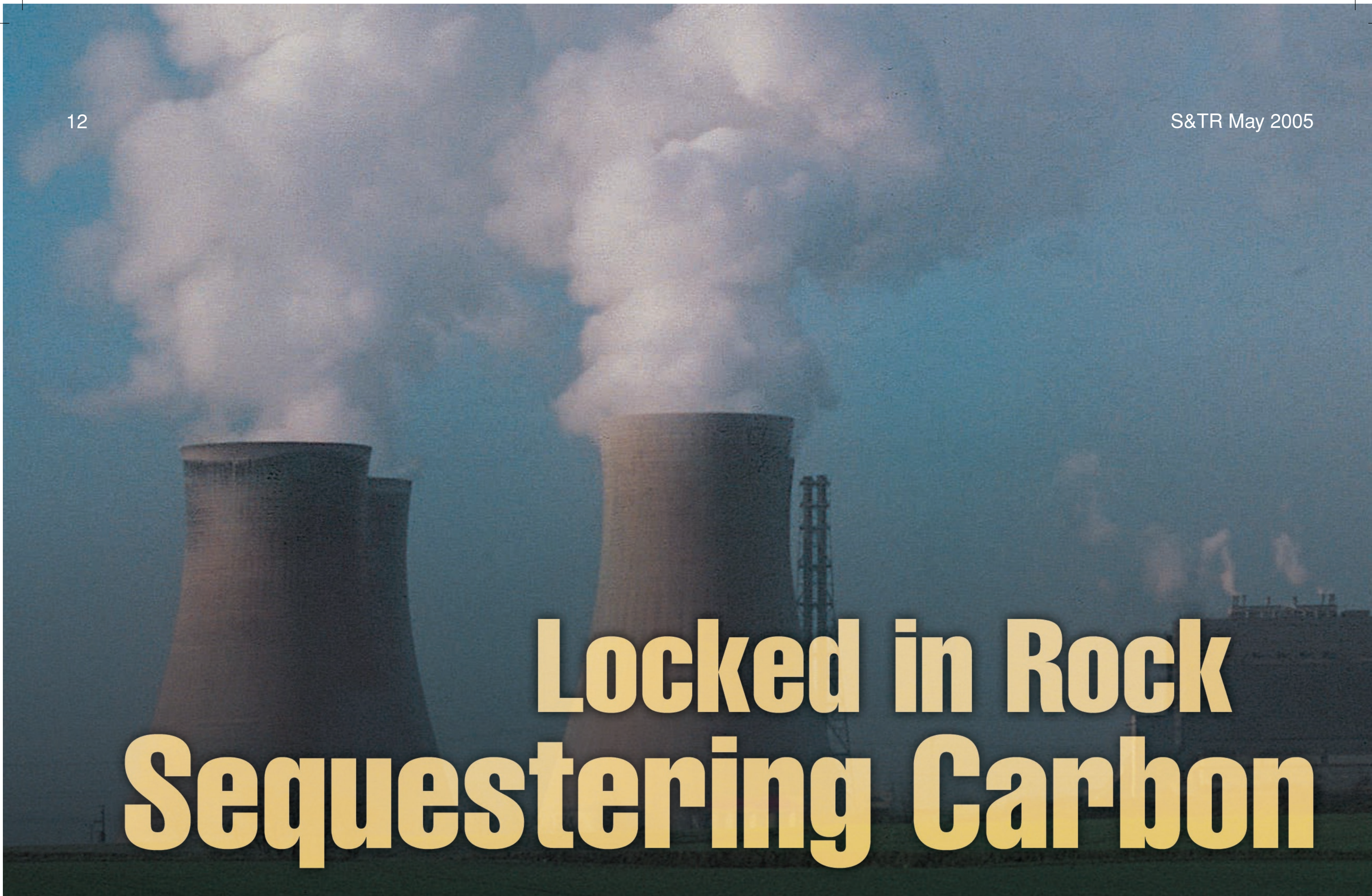
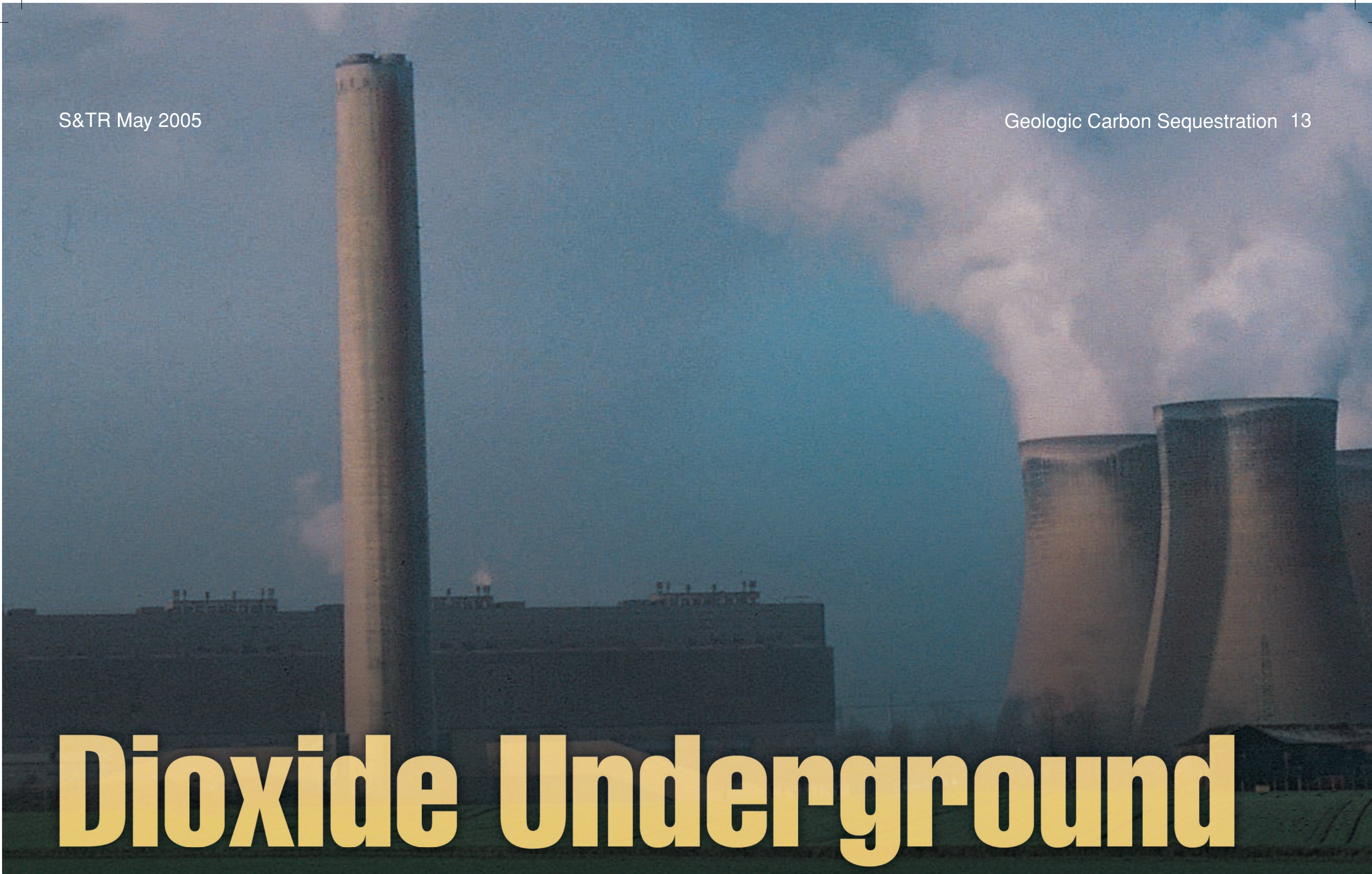


Locked in Rock
Sequestering Carbon

To help reduce atmospheric concentrations of carbon dioxide, researchers are investigating ways to bury it deep underground.

FOR more than a century, scientists have measured a steady buildup of greenhouse gases in the atmosphere as a result of burning fossil fuels. The accumulation of these gases in the upper atmosphere traps solar radiation, which then increases Earth's atmospheric and oceanic temperatures. Many research studies indicate that this continued rise in temperatures will adversely affect Earth's climate, which could lead to dramatic—even catastrophic—changes in weather patterns around the world.

By far, the most abundant greenhouse gas is carbon dioxide (CO_2). Many climate research studies focus on developing technologies to greatly reduce the atmospheric levels of CO_2. One approach being considered to help mitigate CO_2 concentrations is geologic carbon sequestration. With this technique, CO_2 emissions are captured from sources such as power plants and refineries and injected into underground formations—for example, old oil or gas fields or deep,

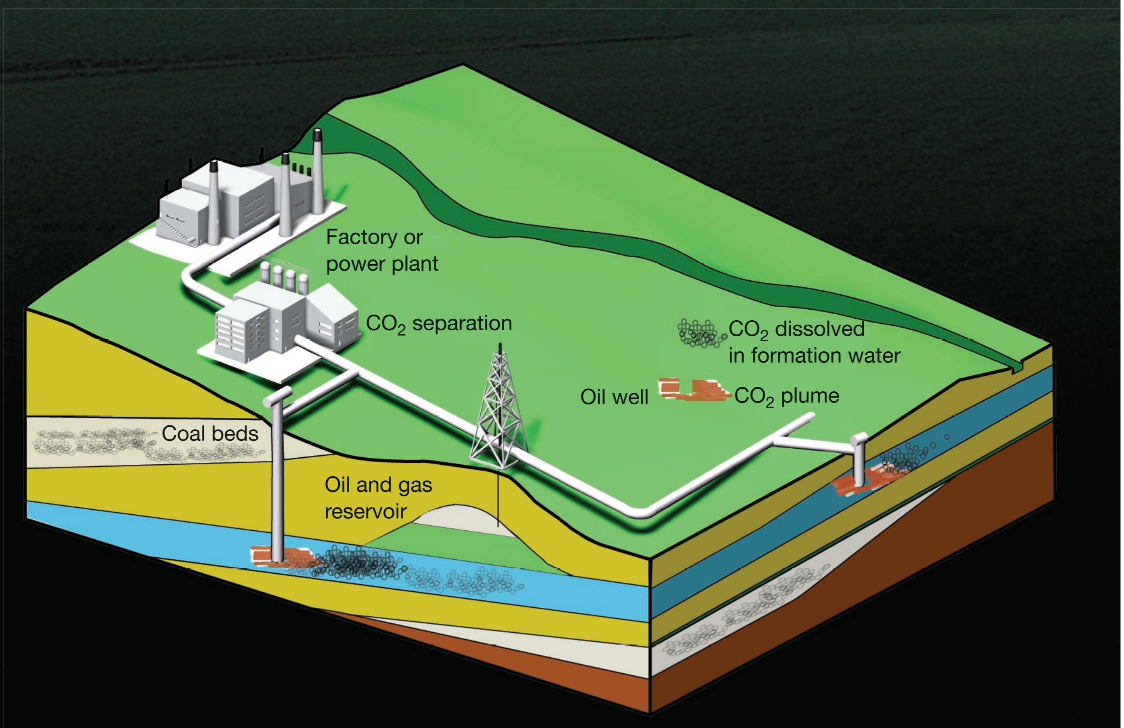


Dioxide Underground

briny aquifers—where the gas can be permanently isolated.

Lawrence Livermore research on geologic sequestration combines fieldwork, laboratory experiments, and modeling and includes scientists and engineers from the Laboratory's Energy and Environment (E&E), Engineering, Chemistry and Materials Science, and Computation directorates. For example, one project is developing methods to capture CO_2 at smokestacks. Another project is helping monitor CO_2 movement after the gas has been injected underground. Laboratory scientists are also studying the safety of carbon sequestration and how CO_2 injection affects a formation's geophysical and geochemical properties. Computer simulations of sequestration techniques will also help decision makers evaluate potential storage sites across the nation.

The carbon sequestration effort receives funding from various sources, including Livermore's Laboratory Directed Research and Development



One approach to help stem the increase of carbon dioxide in Earth's atmosphere is to capture it at the source and inject it into underground formations.

(LDRD) Program, the Department of Energy (DOE), and international energy companies. The Laboratory's research is part of a DOE effort to understand the behavior of CO_2 when stored underground and to develop technologies that make carbon sequestration an effective, cost-competitive, and environmentally benign approach to help solve this worldwide problem. (See the box on p. 15.)

Conservation Is Not Enough

"Reducing energy consumption would help cut CO_2 emissions, but not nearly to the degree we need," says Livermore scientist Julio Friedmann, who leads the Carbon Storage Initiative for the E&E Directorate. "For the foreseeable future, the U.S. and the world will remain dependent on burning fossil fuels." Given this assumption, many scientists believe that safe storage of CO_2 in benign form is a more realistic approach to limit the amount of emissions.

Friedmann and Thomas Homer-Dixon, program director of the Trudeau Centre for Peace and Conflict Studies at the University of Toronto, analyzed the problem in the November/December 2004 issue of *Foreign Affairs*. In that paper, they compared the accumulation of greenhouse gases to the problems cities faced with trash and sewage a hundred years ago. "Like trash, carbon dioxide can be sequestered. Trees and plants already do it: they absorb the gas and turn it into leaves, wood, and roots. But to make a dent in global warming, massive amounts of carbon need to be stored away for a long time—at least a few hundred years—and trees and plants are not up to the task." [*Foreign Affairs* 83(6), pp. 78–79.]

Each year, human activities emit 25-billion tons of CO_2 into the atmosphere. About 2- to 3-billion tons of this annual output is absorbed by forests. Another 7-billion tons is absorbed by the ocean, which could conceivably store even larger amounts of CO_2. (See *S&TR*, May 2004, pp. 20–22.) However, CO_2 can make water acidic, prompting concerns about its long-term effect on marine life.

Preliminary estimates indicate that geologic formations could store many decades' worth of CO_2 emissions safely. "By 2050, nations could be burying 5- to 10-billion tons of CO_2 every year," says Friedmann. "We think Earth's crust could handle that."

CO_2 Already Captured, Stored

Friedmann points out that scientists already know how to capture CO_2 and inject it underground. Since the 1930s, manufacturers have extracted CO_2 from factory emissions and used it to process food and make dry ice. For the past three decades, U.S. oil companies have also injected CO_2 underground to increase production from oil and natural gas wells, a process called enhanced oil recovery. Indeed, the U.S. leads the world in enhanced oil recovery technology, using about 32-million tons of CO_2 per year for this purpose. In addition, Friedmann says, "Enhanced oil recovery represents an opportunity to sequester carbon at a lower cost, compared with storing it in geologic repositories that do not contain fossil fuels. Sales of the recovered oil and gas would generate revenues to help offset the expenses of sequestration."

For safe, long-term storage, CO_2 must be injected more than 800 meters below Earth's surface. At that depth, CO_2 becomes a supercritical fluid, in which it is neither liquid nor gas. Supercritical CO_2 is more dense than CO_2 gas and thus would require less storage volume. Supercritical CO_2 is also less mobile and has a higher solubility underground, which would make sequestration more effective.

Once injected, the supercritical CO_2 begins to displace the oil, brine, or other fluids in underground formations. After several weeks, some of it dissolves into natural gas or oil or becomes trapped in tiny rock pores. One concern is that CO_2 injection changes the pressure in an underground reservoir. If the pressure increases too much, it could reactivate faults or fracture the overlying rock layer, or caprock. These events could lead to CO_2 leakage, compromising the storage effectiveness and possibly posing risks to the environment and human health.

"We know how to capture CO_2 and put it underground, but we also want to understand how carbon injection on a massive scale might affect the geology of an area," says Friedmann. Livermore's focus is on characterizing and quantifying these risks. To do that, researchers must conduct experiments and simulations at several measurement scales, from examining rock pores in microscopic detail to modeling geologic reservoirs many kilometers wide and deep.

Capture Comes First

Before CO_2 can be sequestered, it must be captured from a waste stream, typically a smokestack at a factory or power plant. One economic barrier is the high cost of technologies for the capture process. Developing techniques that can be used at existing power plants is especially challenging because the new processes must be easily integrated with old equipment.

Livermore researchers are pursuing capture techniques that do not create a secondary waste stream and will minimize costs. For example, an LDRD project led by engineer Kevin O'Brien is developing polymeric membrane technology, which is a spin-off from the precision techniques developed to fabricate laser targets for the National Ignition Facility at Livermore. The process, called SLIP (for solventless vapor deposition combined with in situ polymerization), uses nanotechnology to engineer membranes by aligning and polymerizing individual molecules on membrane surfaces. It produces uniform, ultrathin-film membranes that require significantly less separation power and exhibit much greater selectivity than conventional membranes. The Livermore team is collaborating with a consortium

A Long-Term Investment for a Healthy Future

The Department of Energy (DOE) is leading the nation's effort to better understand the geochemical and geomechanical forces underlying carbon sequestration and to develop technologies for long-term carbon storage on a large scale. DOE has created a network of seven public- and private-sector Carbon Sequestration Regional Partnerships to determine which approaches are best suited for different regions of the country. In announcing the initiative in 2002, DOE Secretary Spencer Abraham called the partnerships "the centerpiece of our sequestration program." The partnerships include more than 150 organizations in 40 states, 3 Indian nations, and 4 Canadian provinces.

Lawrence Livermore is a member of the West Coast Regional Carbon Sequestration Partnership, which is led by the California Energy Commission and includes representative organizations from Alaska, Arizona, California, Nevada, Oregon, and Washington. Livermore researchers are helping to investigate potential geologic storage sites in the western U.S.

DOE's Teapot Dome oil field in Wyoming, which is also known as Naval Petroleum Reserve No. 3, will serve as a field laboratory for carbon dioxide (CO_2) storage and monitoring experiments. As part of the project, CO_2 gas will be injected into Teapot Dome fields to boost oil production, and researchers will evaluate technologies for both sequestration and enhanced oil recovery. Livermore geologist Julio Friedmann is the program's senior scientific coordinator, and several Laboratory investigators are developing measurement, monitoring, and verification techniques for the project.

With a potential surface area spanning 130 square kilometers, the Teapot Dome project could grow to be one of the largest sequestration demonstrations in the world. Anadarko Petroleum Corporation has built a 200-kilometer pipeline that moves by-product gas from a natural gas processing plant at Shute Creek in western Wyoming to the Teapot Dome site. Anadarko plans to inject about 7,200 tons a day of CO_2 gas into the declining, century-old Salt Creek field, which amounts to an annual output of about 2.6-million tons of CO_2 that would otherwise be vented into the atmosphere. The CO_2 pumped into the ground will push an additional 30,000 barrels of oil to the surface each day—totaling six times the current production level from the Salt Creek field. Carbon dioxide injection began in 2005 and will continue for several years.

Another DOE project is evaluating sequestration in the Frio formation in the South Liberty field near Houston, Texas. Livermore is collaborating with many institutions on the Frio Brine Pilot Test, which is led by the University of Texas.

In addition, DOE is planning several geologic storage demonstrations. The largest and most ambitious of these is the FutureGen Initiative, whose goal is to build a 275-megawatt zero-emission power plant that generates electricity and hydrogen from coal. The plant, announced by President George W. Bush in 2003, will be designed to capture and store CO_2, making it the world's first coal-fueled prototype power plant to incorporate carbon sequestration technologies. The projected cost of this project is $1 billion, but the plant's location has yet to be determined. When operational, the prototype will be the cleanest fossil fuel–fired power plant in the world.

The U.S. is also cooperating with other nations to advance carbon sequestration technologies. In 2003, DOE, the U.S. State Department, and ministries from 16 nations formed the Carbon Sequestration Leadership Forum to discuss technical and policy issues relating to geologic and other forms of carbon sequestration.

Many nations, including Norway, Canada, Australia, Germany, and the Netherlands, are pursuing large sequestration projects, many of which are associated with the forum. Livermore researchers are also collaborating on some of these international projects. Friedmann, for example, serves as an advisor to a European Union sequestration project in Germany called CO_2SINK.

The CO_2 Capture Project, an international effort funded by eight of the world's leading energy companies, is addressing methods to reduce greenhouse-gas emissions in a manner that contributes to an environmentally acceptable and competitively priced energy supply for the world. Livermore researchers are supporting the project with advanced simulations.

Teapot Dome in Wyoming is a potential site for a large-scale sequestration demonstration that is part of the Department of Energy's study on the effectiveness of storing carbon dioxide deep underground.

of other national laboratories, private industry, and universities to develop and deploy full-scale membrane systems based on SLIP and other technologies.

Another novel approach uses limestone as a CO_2 separation and sequestration strategy. This effort, which is led by chemist Greg Rau from the University of California at Santa Cruz, takes advantage of accelerated weathering of limestone (AWL). AWL treats waste CO_2 with water to produce a carbonic acid solution. The solution can then be neutralized with limestone, thereby converting the original CO_2 gas to bicarbonate.

AWL could be an ideal separation process for coastal power plants because bicarbonate can be safely injected into the ocean. Rau's team is developing an AWL technique that uses the water coproduced with oil or natural gas. Because of the surface-water discharge restrictions associated with oil and gas production, this by-product water must be reinjected. If the AWL technique is successful, it would effectively treat both the water and the CO_2.

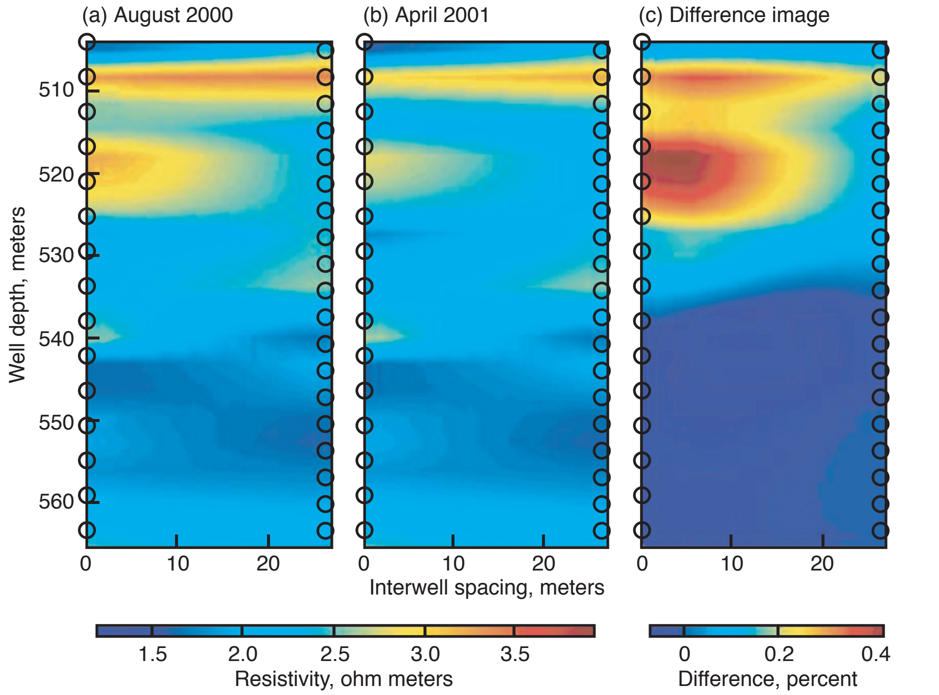
Monitoring Sequestered CO_2

Livermore researchers also have developed techniques to monitor the CO_2 injected underground and ascertain its location. "We need to show that the CO_2 goes down and stays down," says Friedmann.

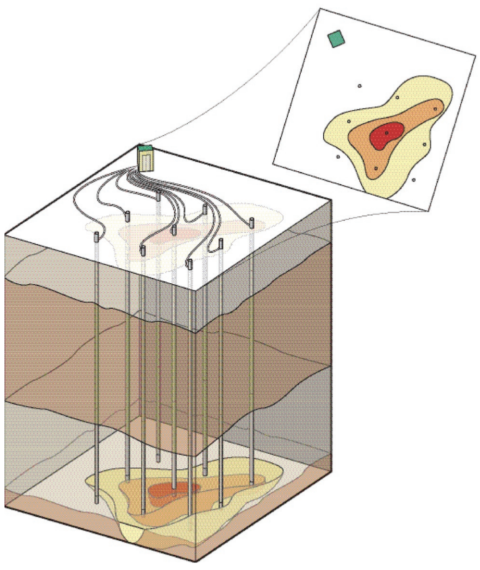
Physicist Barry Kirkendall has demonstrated crosswell electromagnetic (EM) imaging of CO_2 sequestration at the Lost Hills field in central California—an enhanced oil recovery site operated by Chevron USA. The project combines laboratory and field data to develop image interpretation techniques that discriminate between oil, CO_2, and water phases.

The technology, originally developed by researchers at Lawrence Livermore and Lawrence Berkeley national laboratories and scientists at Schlumberger Corporation, takes advantage of the differences in how EM fields are induced in various materials. A transmitter is deployed in one well and a receiver in a second well to measure the electrical resistivity or conductivity of geologic media between the two holes. The resulting data provide a detailed, two-dimensional map of the subsurface resistivity at multiple frequencies between the wells.

A related technology, called electrical resistivity tomography (ERT), works like the computed tomography scans used in medical diagnostics, but instead, it reconstructs the subsurface



Two-dimensional crosswell electromagnetic images show the plane between two observation wells at a site that uses CO_2 injection to enhance oil production. Circles on the left side of each image represent wells with a receiver antenna, and circles on the right side represent wells with a transmitting antenna. Blue shows water in place, yellow is moving oil, and red is moving CO_2. Data were recorded (a) after waterflooding but before CO_2 injection and (b) three months after CO_2 injection. (c) The composite image, which shows the results when data in (a) are subtracted from data in (b), indicates that CO_2 is entering the area at the top left.



This schematic shows the well spacing for an electrical resistivity tomography experiment, which measures the electrical resistivity distribution in the subsurface. Steel casings in old oil wells are used as long electrodes about 1,000 meters deep. Electrical current is driven between two casings, and the resulting voltage distribution is measured on the remaining casings. The process is then repeated with other pairs of wells until electrical properties have been sampled over the entire subsurface volume.

electrical resistivity distribution in three dimensions. Livermore engineers Bill Daily and Abe Ramirez originally developed ERT for environmental research—an effort initially funded by LDRD. Daily has now extended the technology to oil-field applications, such as monitoring sequestered CO_2.

One implementation of Daily's concept used the steel casings of production wells as electrodes extending about 1,000 meters deep. In this approach, which is called long-electrode ERT, electrical current is driven between two of the casings, and the resulting voltage distribution is measured at the remaining casings. This process is then repeated using different wells as the electrode pairs, until the electrical properties of the entire subsurface have been sampled. Results from field trials conducted at oil fields in California, New Mexico, and Wyoming indicate that long-electrode ERT is an effective method for measuring the movements of oil, water, and gas.

Crosswell EM and ERT complement traditional seismic imaging, which uses sound waves to map underground geologic strata. Seismic imaging, however, has a limited capability in distinguishing oil from other fluids such as CO_2. Livermore physicists Brian Bonner and Jim Berryman are investigating whether broadband seismometers, which can record the low-frequency data associated with fluid movement, could be used to map the migration of injected CO_2 over time.

Techniques are also needed to warn operations personnel should CO_2 begin to leak from a storage site. One approach, under investigation by geochemist Greg Nimz and physicist Bryant Hudson, uses noble gas isotopes dissolved in the CO_2 to trace its movement. Noble gases are chemically inert and environmentally safe, and they are persistent and stable in the environment. According to Nimz, xenon isotopes are particularly suitable for monitoring CO_2 storage operations. Batches of CO_2 with different concentrations of xenon isotopes could be injected at the same site, making each batch identifiable with a single xenon analysis.

Remote sensing is another technology that may be useful in detecting CO_2 leakage. For example, Laboratory physicist Bill Pickles has developed a technique using airplanes equipped with hyperspectral cameras, which provide more information than traditional remote-sensing units do. In analyzing images taken during flights over a study area, Pickles found evidence of plant stress caused by high concentrations of CO_2 in the soil. (See *S&TR*, May 2003, pp. 12–21.) He has applied this approach successfully at natural sites, such as Mammoth Lakes, California, and at CO_2 injection sites, such as oil fields in Rangely, Colorado. Ultimately, future space-based platforms might directly monitor CO_2 flux from the surface.

Studying Sequestration Risks

Scientists are concerned that even slow, small releases of CO_2 over many years could significantly reduce the efficacy of carbon storage and could even pose risks to the environment and human health. Studies indicate that faults in the caprock are the natural path for subsurface fluids to slowly escape to the surface, especially when a reservoir is overpressurized. According to Friedmann, the risks of CO_2 leakage are not serious. "Almost all of the risks associated with leakage can be prevented by carefully analyzing the site and downhole pressure data," he says. In addition, any leaks are likely to be detected early by standard monitoring techniques and remediated.

The worst-case scenario is that CO_2 might escape from an injection well that was completely open to the surface, perhaps because the well's seal failed. "A drilled well could be a faster conduit for CO_2 than tiny fissures," says Friedmann.

To study the environmental risk from such an event, Livermore meteorologist Frank Gouveia and geologist Mackenzie Johnson collected field data at Crystal Geyser in Utah in October 2004. Crystal Geyser is an ideal site for evaluating CO_2 leakage because it mimics the worst-case scenario.

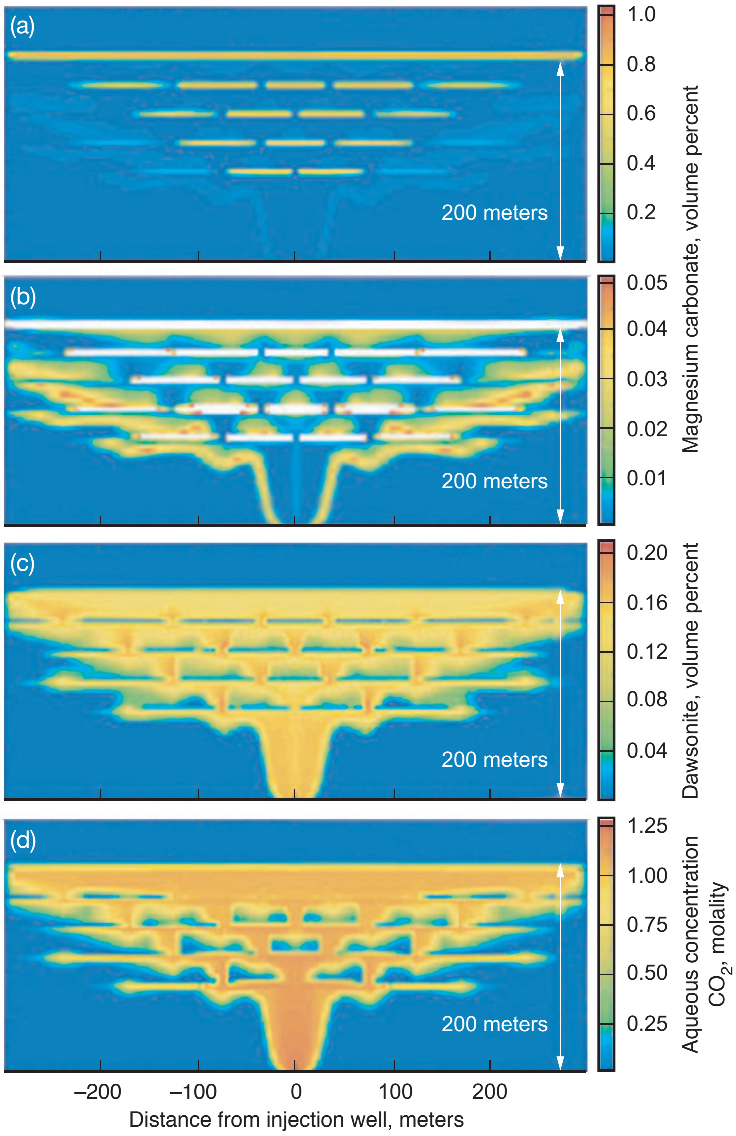
The geyser first erupted in 1936, when a wildcat well being drilled more than 800 meters deep intersected a CO_2-charged aquifer. Today, the geyser erupts

Geologist Mackenzie Johnson collects CO_2 samples and meteorological data at Crystal Geyser, Utah, as part of a two-day field experiment conducted in October 2004.

intermittently as a result of pressure changes in the aquifer. Because this is an artesian well—that is, water flowing into the well is driven by hydrostatic pressure in the aquifer—the CO_2-charged waters naturally flow to the surface. As the water rises in the well, the pressure decreases, and explosive degassing of dissolved CO_2 results. The process is repeated because the CO_2-charged waters continue to flow naturally to the surface.

For the field study, Gouveia and Johnson camped near the geyser for two days, collecting CO_2 samples at different distances from the geyser and recording meteorological data for the area. Five eruptions occurred during the 48-hour period, with eruptions lasting from a few minutes to more than two hours. Geochemist Roald Leif measured the samples when they were returned to Livermore. The results showed that, even just a few meters from the gushing geyser, CO_2 levels were well below human health and safety concerns. "Even very low winds are sufficient to mix the CO_2 quickly," says Gouveia.

A larger team of Livermore researchers plans to return to Crystal Geyser to test various detection and monitoring technologies. The team also will collect data to construct vertical profiles of the CO_2 plume emitted by the geyser.



Using results from CO_2 injection at the Sleipner site in the North Sea, Livermore scientists simulated geochemical trapping mechanisms in a CO_2-flooded saline aquifer after 10 years of flooding followed by 10 years of no flooding. The model predicts the distribution of magnesium carbonate (magnesite) (a) among the aquifer's caprock and thin interbedded shales and (b) along the aquifer's upper and lateral plume boundaries. The model also predicts (c) the concentration distribution of intraplume dawsonite and (d) the extent to which injected CO_2 dissolves into formation waters.

Simulations Lead the Way

Guiding much of the sequestration experiments and fieldwork are simulations designed by a team of computational scientists led by geochemist James W. Johnson. Johnson's team has produced the first reactive transport models of CO_2 injection and sequestration within geologic formations. These simulations show how CO_2 moves through a geologic formation, displacing ambient water, with which it is largely unmixable, and rising relative to this water, owing to its lower density. As the CO_2 plume migrates, some of it precipitates as carbonates in a process called mineral trapping, and some dissolves in the underground water, called solubility trapping. Some CO_2 is eventually isolated within rock pores bound by the overlying caprock, which is typically composed of shale—a process called hydrodynamic trapping.

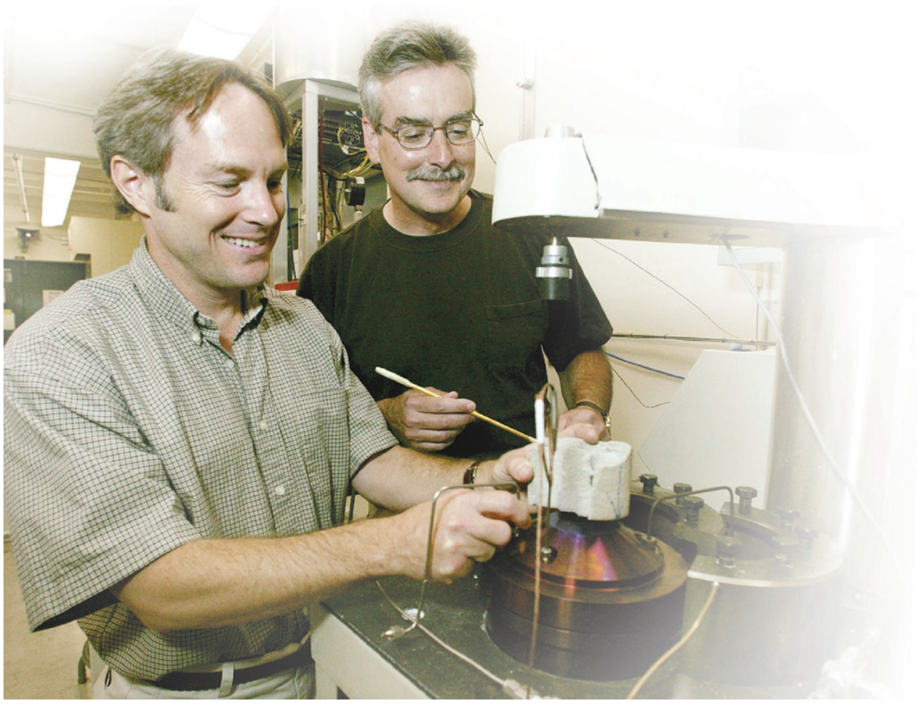
The Livermore team used these models to evaluate a sequestration operation for Norway's state oil company, Statoil. Each year, Statoil injects about 1-million tons of CO_2 recovered from its offshore Sleipner site into a saline geologic formation under the North Sea. The amount of CO_2 being sequestered is equivalent to the output of a 150-megawatt coal-fired power plant. Statoil pursued the sequestration effort after Norway imposed a federal tax on atmospheric CO_2 emissions from combustion-based sources. The Sleipner site is the first and largest commercial CO_2 geologic sequestration facility in the world, and it is proving to be both environmentally and financially sound.

In analyzing the Sleipner site, Johnson's team developed a suite of computational tools to identify the geochemical, hydrologic, and structural constraints for successful geologic CO_2 sequestration. (See *S&TR*, December 2000, pp. 20–21.) This modeling software includes NUFT, a reactive transport simulator developed by Livermore physicist John Nitao; GEMBOCHS, the supporting geochemical software and databases developed by Johnson; and LDEC, a geomechanical model developed by Laboratory physicist Joe Morris. Reactive transport modeling integrates the processes that characterize dynamic geologic systems, including chemical reactions, fluid flow, heat transfer, and mechanical stress and strain. Because these processes are interdependent, they must be modeled simultaneously for the simulations to show the true behavior of geologic systems.

"We learned a lot from studying the Sleipner site," says Johnson. "It showed us how CO_2 moves underground, where and when it becomes trapped, and the relative effectiveness of distinct trapping mechanisms." The team also studied the integrity of the caprock in a project funded by the energy industry–supported CO_2 Capture Project. "We discovered that two opposing processes—geochemical and geomechanical—act on microcracks in the caprock." Geochemical processes, mainly the formation of carbonates when CO_2 reacts with minerals, help to seal caprock fractures. However, geomechanical processes work in the opposite direction, forcing some microcracks to widen as the injected CO_2 increases the pressure underground.

In an LDRD project, Johnson and Livermore geochemist Kevin Knauss are performing integrated laboratory and modeling experiments to verify key geochemical predictions of the Sleipner work. These experiments are expected to confirm that CO_2 interaction with typical shale caprock forms carbonates containing magnesium, iron, and calcium. The experiments are also investigating the potential importance of dawsonite—carbonate containing sodium and aluminum, which may precipitate through CO_2 interaction with typical sandstone reservoirs.

Johnson, Nitao, and others are expanding their simulation capabilities to model in three dimensions. Three-dimensional modeling will allow researchers to examine injection scenarios in detail, including those involving enhanced oil recovery, and to "test" monitoring tools in a virtual environment before expensive prototypes are built. So far, says Johnson, "Our simulation results have been very encouraging for carbon sequestration technology."



Geochemists James W. Johnson (left) and Kevin Knauss test a sample of sandstone from the Frio formation in the South Liberty field near Houston, Texas.

Sound Data for Decision Makers

"The Earth's crust is complex and heterogeneous, but we're gaining a good understanding of what happens when we inject CO_2 deep underground," says Friedmann. "The bottom line is that geologic storage appears to be a safe, reliable, and permanent means to help mitigate the buildup of greenhouse gases." He acknowledges, however, that much more research is required to provide a sound basis for the U.S. and other governments to make important policy and economic decisions about carbon capture and sequestration.

Large-scale sequestration will require significant, long-term investments of governmental and industrial resources. National laboratories such as Lawrence Livermore play a vital role in providing the science and technology needed to support these investments. Livermore researchers are meeting the challenge—using their combined expertise in such diverse fields as geophysics, chemistry, engineering, and computer modeling to help mitigate the effects of greenhouse-gas emissions.

What they're finding is that, for once, burying a problem might be a good solution.

—Arnie Heller

Key Words: carbon sequestration, Carbon Storage Initiative, climate change, crosswell electromagnetic (EM) imaging, electrical resistivity tomography (ERT), FutureGen Initiative, GEMBOCHS, global warming, hyperspectral cameras, LDEC, NUFT, reactive transport modeling, SLIP (solventless vapor deposition combined with in situ polymerization) process, Teapot Dome.

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